

Intrinsic Superconductivity at 25 K in Highly Oriented Pyrolytic Graphite

P. Esquinazi,^{1,2,3,*} N. García,^{3,1,†} J. Barzola-Quiquia,¹ J. C. González,³
M. Muñoz,³ P. Rödiger,¹ K. Schindler,¹ J.-L. Yao,¹ and M. Ziese¹

¹Abteilung für Supraleitung und Magnetismus, Institut für Experimentelle Physik II,
Universität Leipzig, Linnéstraße 5, D-04103 Leipzig, Germany

²CMAM, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain

³Laboratorio de Física de Sistemas Pequeños y Nanotecnología,
Consejo Superior de Investigaciones Científicas, E-28006 Madrid, Spain

High resolution magnetoresistance data in highly oriented pyrolytic graphite thin samples manifest non-homogenous superconductivity with critical temperature $T_c \sim 25$ K. These data exhibit: i) hysteretic loops of resistance versus magnetic field similar to Josephson-coupled grains, ii) quantum Andreev's resonances and iii) absence of the Schubnikov-de Haas oscillations. The results indicate that graphite is a system with non-percolative superconducting domains immersed in a semiconducting-like matrix. As possible origin of the superconductivity in graphite we discuss interior-gap superconductivity when two very different electronic masses are present.

PACS numbers: 74.10.+v, 74.45.+c, 74.78.Na

The standard way to ascribe superconductivity to materials is by observing the screening of an external applied magnetic field, the Meissner effect, below a critical field B_{c1} and, although less important from the physical point of view, by measuring the drop of resistance to practically zero below a critical temperature T_c . These phenomena are observed for percolative or homogenous superconductors where a macroscopic wave function of the Cooper pairs exists [1]. It is well known that in inhomogeneous superconducting samples, as for example the well-known ceramic high T_c oxides, sometimes superconductivity does not percolate, then the resistance does not drop to zero and the Meissner effect is small. In this case the criteria to assign non-percolative inhomogeneous superconductivity to a material is much less obvious. In addition, we would like to discuss here a superconducting high- T_c material with a very low density of free electrons or quasiparticles $n \lesssim 10^{18} \text{ cm}^{-3}$, with very different effective masses m^* . We think that this is the case of highly oriented pyrolytic graphite (HOPG), the material studied in this work.

Untreated HOPG samples manifest large electronic mean free path and Fermi wavelength of order of microns [2]. On the other hand the same samples reveal that the surface is not an equipotential with metallic and insulating regions that can move [3, 4]. It seems clear that the view of graphite as a more or less ordered, homogeneous system and with a homogeneous density of carriers cannot be hold and it does not represent the interesting piece of the physics of HOPG. Although resistance $R(T)$ data can be fitted, in some cases, with a homogeneous two band model (TBM) using two mobilities and two carrier concentrations (all temperature dependent parameters) [5], there are other observations as a function of the applied magnetic field reported here that cannot be explained within this model. In this work we treat HOPG as a non-uniform electronic system and as such it will be

discussed.

To aboard this hard problem we have obtained over 10^6 high resolution magnetoresistance (MR) data points in a range of temperatures. These data exhibit: (i) irreversible hysteretic loops of resistance versus magnetic field similar to those observed in granular superconductors with Josephson-coupled grains [6, 7] that can be assigned to superconducting fluxons, (ii) quantum Andreev's resonances in the MR [8] and (iii) absence of Schubnikov-de Haas (SdH) oscillations. The experimental data indicate the existence of energy gaps at the Fermi level and that HOPG is a non-percolative superconductor with "granular" domains immersed in a semiconductor-like matrix. The origin of the superconductivity in graphite may be assigned to interior-gap superconductivity that predicts a gapless stability when two different masses are present, a problem that has been discussed by Liu and Wilczek [9].

The high-resolution, low-noise four-wires MR measurements have been performed by AC technique (Linear Research LR-700 Bridge with 8 channels LR-720 multiplexer) with ppm resolution and in some cases also with a DC technique (Keithley 2182 with 2001 Nanovoltmeter and Keithley 6221 current source). The temperature stability achieved was ~ 0.1 mK and the magnetic field, always applied normal to the graphene planes, was measured by a Hall sensor just before and after measuring the resistance, and located at the same sample holder inside a superconducting-coil magnetocryostat. We used currents between $1 \dots 100 \mu\text{A}$.

To start with our strategy we have prepared different samples of HOPG that just differ in its ordering and size and they exhibit apparently different behaviors with T. Figure 1 shows $R(T)$ for the samples indicated in the figure caption. Usually one tends to fit these curves with the TBM. In particular the $R(T)$ of sample (3) can be fitted approximately. However, carriers in HOPG have two

different masses and one of them is practically zero corresponding to Dirac electrons [10]. Furthermore, there are other important aspects described below that undoubtedly cannot be put into accord with the TBM. We concentrate in the very thin and micrometer small sample because it should have less number of fluctuating domains and this should provide more clear superconducting-related effects. Note that this sample shows a semiconducting like behavior that levels off at $T \simeq 25$ K; its in-plane resistivity $\rho_{ab}(10$ K) $\simeq (50 \pm 10)$ $\mu\Omega\text{cm}$ is similar to the one of sample (1) from which it has been obtained by careful exfoliation.

Figure 2(a) shows the MR of sample (3) at 4 K in detail and in the region 4 T to 8 T with larger resolution using a magnetic field step of $\simeq 1$ Oe. The first surprise is that the MR is very small compared with the MR of larger samples of HOPG. In these samples the ordinary MR of HOPG between 0 T and 8 T is $\sim 10000\%$ while in the small sample measured here is only $\lesssim 300\%$. This difference is discussed in Ref. 2. In addition, SdH oscillations are absent in sample (3) (in other samples of similar size we measured they appear very weak). This might imply that the Fermi level lies in a gap. Notice that we decided to perform experiments with very small field increment. This was not done accidentally. The reason is that we expected to have weak quantum oscillation resonances – compared with the classical SdH oscillations – due to the small number of potential fluctuations (note that the sample is small, of the order or smaller than the mean free path and Fermi wave length) and these fluctuations will induce an oscillating transmissivity through the potential wells. These quantum oscillations were proposed theoretically to interpret observed structures that were over seen or consider noise in graphene samples [8]. And of course the sample of Fig. 2 shows the expected quantum oscillations. These quantum oscillations have a two period spectrum indicating that in the sample one has at least two characteristic potential wells. Figure 2(b) shows the oscillation amplitude of the two harmonics (see also the inset) as a function of T , which remain constant below 10 K and vanish at a critical temperature $T_c \simeq 25$ K.

We claim that these oscillations, given their small amplitude of ~ 100 nV...400 nV (much smaller than the corresponding values in temperature for the used range $T \geq 2$ K) are due to the interference of wave functions that suffer Andreev's reflections at the potential walls matching low-gap semiconducting with superconducting regions. From the period of the oscillations in field we can estimate that there are superconducting “granular” domains of size around 1 μm separated by small-gap semiconducting matrix of similar size, which couples the superconducting grains. If this picture is realized one expects to see pinning and dissipation effects due to fluxons, as discussed by Ji et al. in Ref. 6, with circumvent superconducting currents between the superconducting grains through the semiconducting regions. One may

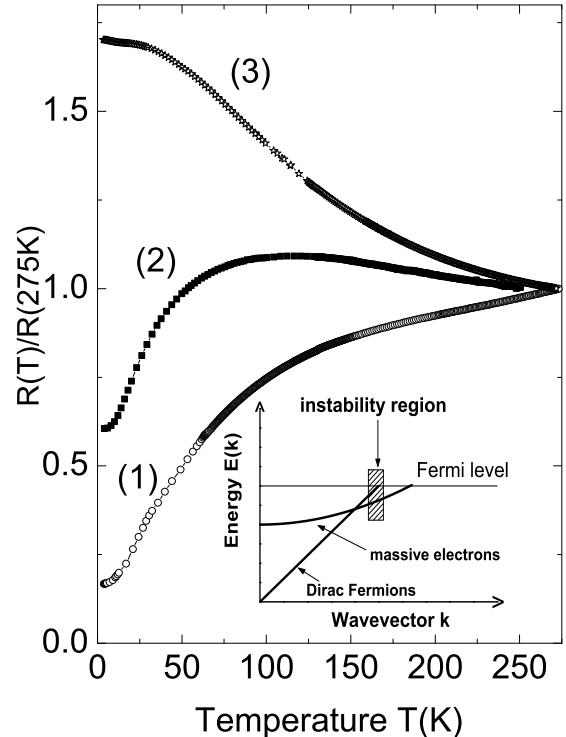


FIG. 1: Normalized resistance as a function of temperature at zero applied field for three HOPG samples. Samples (1) and (3) were obtained from the same HOPG grade ZYA (0.4° rocking curve width) bulk sample from Advanced Ceramics. Particle induced x-ray emission indicates impurity levels of metallic elements below $5 \mu\text{g/g}$ with exception of V ($16 \mu\text{g/g}$). Sample (1) ($R(275 \text{ K}) = 72 \text{ m}\Omega$) was $\sim 10 \mu\text{m}$ thick and 4.4 mm length. Sample (3) ($R(275 \text{ K}) = 16 \Omega$) was 12 nm thick and $\sim 30 \mu\text{m}$ length and width, with $\sim 9 \mu\text{m}$ distance between nearby electrodes, see inset in Fig. 2(a). The Pd-electrodes (to avoid Schottky barriers) were prepared using conventional electron lithography. The sample (2) ($R(275 \text{ K}) = 6.5 \text{ m}\Omega$) was obtained from HOPG grade ZYC bulk sample (3.5°). The inset shows schematically the energy dispersion relations for two carriers in graphite, massive and massless (Dirac fermions). Following Ref. 9, the instability region lies around the Fermi wavevector of the light particles.

argue against the physical ground of the model we are proposing: how is it possible that superconducting pairs can be kept in a micron-size semiconducting-like regions connecting the superconducting ones? This should not be a problem. By using nano-fabricated constrictions and measuring the transition from ohmic to ballistic transport we have observed that the mean free path of the carriers in HOPG at 10 K is $\gtrsim 10 \mu\text{m}$. Therefore, it should be perfectly possible that the pairs travel $\sim 1 \mu\text{m}$ distance without breaking out. In other words the proximity effect in graphite may extend to microns.

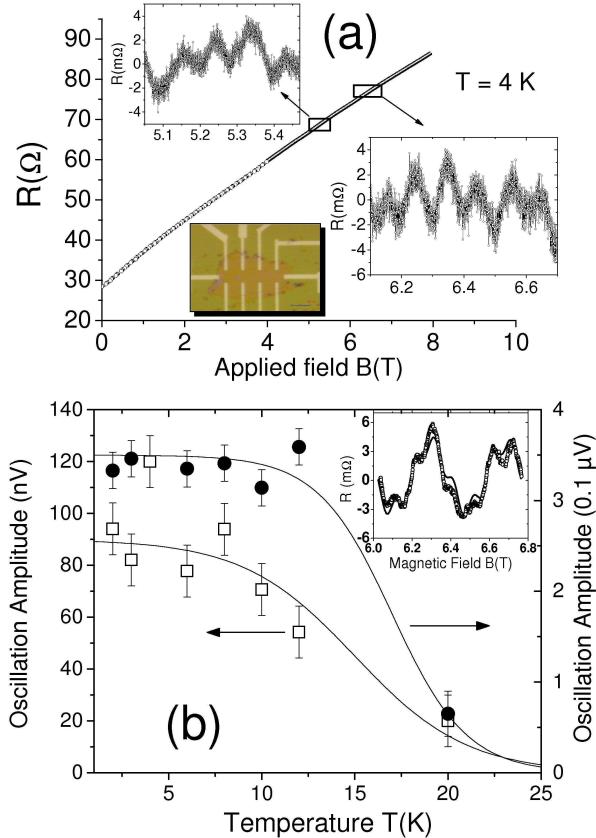


FIG. 2: (a) Resistance of sample (3) between two adjacent voltage electrodes as a function of magnetic field. A close inspection of the MR of this sample at fields above 0.5 T reveals an anomalous behavior, namely the MR oscillates. The oscillations shown in the insets were obtained after subtracting a quadratic field dependence around 5.3 T and 6.4 T. These small-field-period oscillations in the resistance are superposed to oscillations of larger amplitude and field period, see inset in (b). Further measurements indicate that the overall shape, field positions and period are independent of the field sweeping rate, field step and field sweep direction. The oscillations are observed at low as well as high fields, as expected because the slope of R vs. B does not depend appreciable with field [8]. Different periods as well as oscillation amplitudes are observed for other samples. The inset shows an optical microscope picture of the sample with the Pd-electrodes. Counting clockwise from input current electrode 1 at the right, the data shown were taken between electrodes 3 and 4 (Ch.2). (b) Temperature dependence of the voltage amplitude of the two oscillations taken from the Fourier fit, see inset. The continuous lines are a guide. The inset shows the data at 2 K after subtraction of a linear field background and the continuous line is the Fourier fit with periods 0.1 T and 0.387 T. These periods are independent of temperature within experimental resolution.

If there are fluxons then one should have irreversible hysteretic loops of the kind observed in granular superconductors [6, 7]. Figure 3(a) shows this irreversibility that cannot be explained by ferromagnetism, ferroelectricity due to motion of charges or by usual Abrikosov vortices, since no sign of irreversibility has been seen within experimental error for magnetic fields applied parallel to the planes. We have a huge anisotropy in an otherwise a small spin-orbit coupling material. Note that the two minima in R are observed at the positive and negative fields coming from high fields from the same direction. Only by fluxons running between the superconducting and the semiconducting-like regions these hysteresis loops can be explained. For a better appreciation of the hysteresis the inset in Fig. 3(a) shows the difference between the two curves, i.e. the resistance curve obtained by starting at a negative field and sweeping to positive fields is subtracted from the resistance curve measured when starting at a positive field and sweeping to negative fields. The height of the extreme as well as their fields $B_m(T)$ depend on T . The T -dependence of this irreversibility ΔR as well as $B_m(T)$ vanish at $T_i \sim 11. The reason why the irreversible behaviour shown in Fig. 3 vanishes at ~ 11 K in contrast to the ~ 25 K observed from the oscillatory behavior of Fig. 2, can be easily related to the pinning of the fluxons inside the grains. The temperature dependence of the irreversibility in field, continuous lines in Fig. 3(b), follows $(1 - (T/T_i))^{1.5}$ a similar dependence as for the irreversibility line of vortices observed in high-temperature superconductors.$

Because it is just graphite, the superconducting regions have a very small number of free electrons, say $\lesssim 10^{-4}$ electrons per carbon atom [5]. A simple estimate shows that the London penetration length is larger than microns and therefore the Meissner effect should be unnoticeable. Also the resistance does not drop to zero because the superconducting regions do not percolate, in addition to the resistance due to the motion of fluxons. The observed hysteresis is a very strong fingerprint of superconducting fluxons, difficult to rule out.

The density of carriers in HOPG samples is very probably highly inhomogeneous, and upon region in the sample it may be much smaller than $10^{-4}/\text{C-atom}$. What might be the physical origin of this superconductivity? Graphite contains two carrier families with very different m^* , one with a negligible mass called Dirac fermions. Therefore, the ratio between masses may be very large, 100 or larger. These different masses establish large instabilities if the number of the different carriers is not that different. Then we have a large extended band with a large Fermi energy corresponding to the light carriers and a lower Fermi energy for the heavy carriers, see inset in Fig. 1. A large density of the heavy carriers pinned at the Fermi energy of the light particles has strong electron interaction and creates instabilities that will be discussed in other work. In particular for this situation Liu and

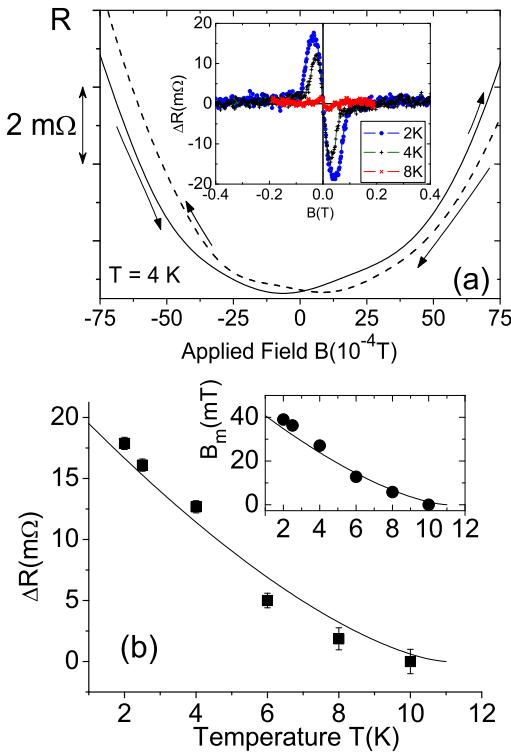


FIG. 3: (a) Strongly enhanced MR curve near zero field. A weak hysteresis appears similar to butterfly MR loops for superconductors with Josephson-coupled grains [6]. For a clear observation of the hysteresis we present in the inset the difference of the resistance curves (see text). (b) The height of the irreversibility maximum ΔR as well as their field positions B_m (see inset) vs. temperature. The continuous lines follow the function $\propto (1 - (T/11))^{1.5}$.

Wilczek [9] have predicted a condensed superfluid state called interior-gap superconductivity or breached superconductivity. Graphite might be a good candidate where some concepts of this theory could be useful. In fact the picture they describe for their theory [9] is similar to that of the inset in Fig. 1. In this theory no gap exists and the material may exhibit *p*-type superconductivity, which has been also discussed for graphite [11] as a more robust state in a non-homogeneous system.

The results of Figs. 2 and 3 belong to a micrometer size sample (parallel to the planes) and 12 nm thickness in order to have few potential fluctuations. Measurements in two other samples of similar size show similar behavior but slightly different T_c 's. In larger samples, as for example the other two reported in Fig. 1, the same type of effects should be seen but more in terms of universal conductance fluctuations. In fact we have observed in these and other larger samples fluctuations in the resis-

tance up to room temperature, however they are difficult to tackle down and their amplitudes change with time, an effect that is probably related to the motion of charges with current and applied magnetic field. Superconductivity in graphite should by no means limited to the 25 K here obtained for the small sample, but depends on the charge density, defect density and the related instabilities at Fermi level.

We note that hints for superconductivity in HOPG samples from SQUID measurements have been invoked in the past [12]. However, resolution limits of the magnetometer and the partial admixture of ferromagnetic-like signals casted doubts on the origin of those signals. Other studies [13] claimed superconductivity in graphite based on the metal-insulator transition observed under a magnetic field, although superconductivity does not necessarily need to be invoked to understand this transition. There is also a theoretical work that claims high- T_c *d*-wave superconductivity in graphite based on resonating valence bonds [14].

Concluding, in this work we have obtained evidence that supports the existence of intrinsic superconductivity in HOPG based on the irreversibility of the MR and on the quantum oscillations. We think that interior-gap – breached superconductivity [9] is an interesting starting concept to understand the observed as well as other phenomena in the transport properties of graphite.

We gratefully thank Y.Kopelevich for fruitful discussions on the superconductivity of graphite. This work was done with the support of the DFG under ES 86/11, the Spanish CACyT and Ministerio de Educación y Ciencia. J.-L. Yao acknowledges the support from the A. von Humboldt foundation.

* Electronic address: esquin@physik.uni-leipzig.de

† Electronic address: nicolas.garcia@fsp.csic.es

- [1] See, for example,. M. Thinkam, *Introduction to Superconductivity* (McGraw-Hill, New York, 1996).
- [2] J. C. González, M. Muñoz, N. García, J. Barzola-Quiquia, D. Spoddig, K. Schindler, and P. Esquinazi, Phys. Rev. Lett. (in press).
- [3] Y. Lu, M. Muñoz, C. S. Steplecaru, C. Hao, M. Bai, N. García, K. Schindler, and P. Esquinazi, Phys. Rev. Lett. **97**, 076805 (2006).
- [4] D. Martinez-Martin and J. Gomez-Herrero, arXiv:0708.2994.
- [5] B. T. Kelly, *Physics of Graphite* (London: Applied Science Publishers, 1981).
- [6] L. Ji, M. S. Rzchowski, N. Anand, and M. Thinkam, Phys. Rev. B **47**, 470 (1993).
- [7] Y. Kopelevich, C. dos Santos, S. Moehlecke, and A. Machado, arXiv:0108311.
- [8] N. García, arXiv:0706.0135.
- [9] W. V. Liu and F. Wilczek, Phys. Rev. Lett. **90**, 047002 (2003), see also M. N. Forbes et al., *idem* **94**, 017001 (2005); L. He et al., Phys. Rev. B **74**, 024516 (2006).

- [10] I. A. Luk'yanchuk and Y. Kopelevich, Phys. Rev. Lett. **93**, 166402 (2004).
- [11] J. González, F. Guinea, and M. A. H. Vozmediano, Phys. Rev. B **63**, 134421 (2001).
- [12] See, for example,, Y. Kopelevich and P. Esquinazi, J. Low Temp. Phys. **146**, 629 (2007), and refs. therein.
- [13] Y. Kopelevich, P. Esquinazi, J. H. S. Torres, R. R. da Silva, and H. Kempa (Springer-Verlag Berlin, 2003), vol. 43 of *Advances in Solid State Physics*, B. Kramer (Ed.), pp. 207–222.
- [14] A. M. Black-Schaffer and S. Doniach, Phys. Rev. B **75**, 134512 (2007).